Staff Report

Use Information and Air Monitoring Recommendation for the Pesticide Active Ingredient Benomyl

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USE INFORMATION AND AIR MONITORING RECOMMENDATION FOR THE PESTICIDE ACTIVE INGREDIENT BENOMYL

A. BACKGROUND

This recommendation contains general information regarding the physical-chemical properties and the historical uses of benomyl. The Department of Pesticide Regulation (DPR) provides this information to assist the Air Resources Board (ARB) in their selection of appropriate locations for conducting pesticide air monitoring operations.

Table 1 describes some of the physical-chemical properties of benomyl.

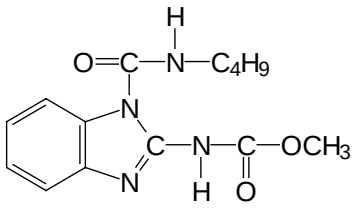
Table 1. Some Physical-Chemical Properties of Benomyl

Chemical name	Methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate
Common name	Benomyl
Some tradenames[†]	Benlate (du Pont),
CAS number	17804-35-2
Molecular formula	$C_{14}H_{18}N_4O_3$
Molecular weight	290.3
Form	Colorless or white crystals with faint acrid odor (Montgomery, 1997; Tomlin, 1994)
Solubility	Water: 2.8 mg/L at 25°C (stable only at pH7) (Montgomery, 1997)
Vapor pressure	3.73×10^{-8} mmHg at 25°C (Kollman and Segawa, 1995)
Henry's Law Constant	5.1×10^{-9} atm-m³/mole at 25°C (calculated)
Soil adsorption Coefficient (Kd)	3.96×10^{1} g/cm³ C (Kollman and Segawa, 1995)
Aerobic soil metabolism half-life	7.92×10^{-1} day (Kollman and Segawa, 1995)
Anaerobic soil metabolism half-life	1.00 day (Kollman and Segawa, 1995)

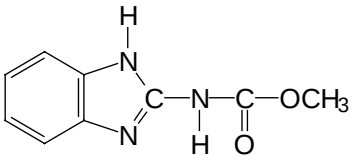
In all environmental compartments, benomyl (figure 1a) decomposes by loss of the butylcarbamoyl group to form the relatively stable, strongly fungicidal methyl 2-benzimidazolecarbamate, also known as carbendazim (figure 1b) (Tomlin, 1994). In soil and water, benomyl rapidly converts to carbendazim and 2-aminobenzimidazole (Montgomery, 1997). Benomyl residues are relatively immobile in organic soils, and were detected only in the top four inches. At least two strains of fungi and four strains of bacteria demonstrated the ability to degrade benomyl to nonfungicidal compounds in loamy soils (Helweg, 1972).

[†] Disclaimer: The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

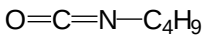
Figure 1. The Chemical Structures of Benomyl, Carbendazim, and n-Butyl Isocyanate



(a) Benomyl



(b) Carbendazim



(c) Butyl isocyanate

In laboratory studies under simulated greenhouse conditions with temperatures ranging from 25°C to 40°C, benomyl decomposed to equimolar amounts of carbendazim and butyl isocyanate (BIC) (figure 1c) when mixed with water and introduced over a layer of basaltic gravel growing medium (Tang et al., 1993; Tang et al., 1992). BIC readily volatilized and was detected in the vapor phase, regardless of formulation. As temperature increased, the rate of BIC formation was enhanced in the early hours following application, especially when the dry flowable formulation was used (Tang, 1993). In a greenhouse study, BIC was detected in air samples collected from sealed glass dishes containing aqueous benomyl suspensions (Aragaki et al., 1994). Airborne concentrations of BIC would likely be lower under field conditions because of the dilution of open air (Tang, 1993).

Benomyl has an LC_{50} (96 hour) of 0.17 mg/L for rainbow trout, and 4.2 mg/L for goldfish. It is nontoxic to bees, with an oral and contact $LD_{50} > 10\mu g$/bee (Tomlin, 1994).

B. USE OF BENOMYL

As of November 1999, two products containing benomyl were registered for use in California. Of the two benomyl products, one is registered for home-garden use, and one product is registered for agricultural use.

Benomyl is a systemic, benzamidazole fungicide that is selectively toxic to microorganisms and invertebrates. It is used to treat a wide range of fungal diseases in field crops, fruit and nut crops, and ornamentals.

In California's agricultural setting, growers primarily use benomyl to control brown rot blossom blight in almonds; botrytis bunch rot, anthracnose, and isarcopsis leaf spot in grapes; and brown rot blossom blight, powdery mildew, and cherry leaf spot in stone fruits. Benomyl recommended label use rates range from 0.5 to 6 pounds per active acre. The benomyl product label recommends use

rates of 3 pounds active ingredient per acre for almonds, and 6 pounds per acre in grapes, stone fruits, and citrus. For almond and stone fruit crops, the label specifies that two applications are necessary for complete control; the first application should be applied at pink bud or popcorn stage, followed by a second application at full bloom stage 10 days later. For grapes, the label specifies application should occur at first bloom, followed by a second application fourteen days later. For all crops, the label specifies that benomyl should not be applied alone, but should be used only in combination or in an alternating application program with a nonbenzimidazole fungicide.

The benomyl product label offers several methods for application, including: chemigation (including center pivot, lateral move, end tow, side wheel roll, traveler, big gun, solid set, or hand move irrigation systems) on beans, carrots, celery, cucurbits, strawberries and tomatoes; air blast field crop sprayers; and air blast tree and vine sprayers. Benomyl is available as a wettable powder and includes the Signal Words "Caution" on the label.

With DPR's implementation of full pesticide use reporting in 1990, all users must report the agricultural use of any pesticide to their county agricultural commissioner, who subsequently forwards this information to DPR. DPR compiles and publishes the use information in the annual Pesticide Use Report (PUR). Because of California's broad definition for agricultural use, DPR includes data from pesticide applications to parks, golf courses, cemeteries, rangeland, pastures, and rights-of-way, postharvest applications of pesticides to agricultural commodities, and all pesticides used in poultry and fish production, and some livestock applications in the PUR. DPR does not collect use information for home and garden use, or for most industrial and institutional uses. The information included in this monitoring recommendation reflects widespread cropland applications of benomyl. Use rates were calculated by dividing the total pounds of benomyl used (where benomyl was applied to acreage) by the total number of acres treated.

According to the PUR, the total amount of benomyl used in California from 1990 to 1998 has ranged annually between slightly more than 114,000 to over 536,000 pounds (Table 2). The majority of California's total benomyl use occurred in five counties—Kern, Madera, Fresno, Tulare, and Merced. Although the annual amounts of benomyl used in the five counties have varied widely since 1991, the use patterns have varied little.

In California, growers use benomyl primarily to control brown rot blossom blight on almonds and stone fruits, and botrytis bunch rots in grapes (Table 3). Treatments usually are made in the late winter and early spring (Table 4). The use of benomyl is difficult to predict as disease pressure is depended on weather and other factors, such as cultural practices. However, assuming that no significant changes in weather will occur next year, the use of benomyl is not expected to change.

Table 2. Annual Cropland Use of Benomyl by County (Pounds of Active Ingredient)

County	1990	1991	1992	1993	1994	1995	1996	1997	1998
Kern	7,899	4,225	10,596	8,782	16,625	29,616	15,595	17,375	56,911
Madera	11,357	7,658	9,119	309,825	12,311	15,434	21,659	15,189	38,100
Fresno	30,366	21,884	26,077	31,199	30,412	33,190	15,691	12,902	25,827
Tulare	19,796	17,937	18,685	19,804	20,074	26,675	11,993	9,248	20,977
Merced	6,220	4,896	4,458	4,769	9,372	13,232	16,416	13,779	19,520
Stanislaus	2,615	2,313	803	2,063	3,210	6,227	10,099	3,621	8,232
Ventura	6,851	7,100	10,301	106,771	5,928	9,318	7,257	6,159	7,642
Mendocino	2,163	1,393	1,743	2,781	1,421	2,616	2,266	3,184	5,068
Lake	273	69	30	619	306	1,998	1,075	1,442	4,604
Monterey	10,832	8,687	5,716	7,268	5,864	4,157	3,372	3,247	3,874
Santa Barbara	4,331	3,335	2,662	2,248	2,094	3,978	4,289	3,070	3,678
San Joaquin	4,455	2,425	1,332	1,811	3,058	1,227	1,874	1,707	3,551
Sacramento	3,213	901	768	593	32	501	603	1,273	3,430
Orange	3,408	2,093	3,050	405	1,243	2,095	1,139	1,512	2,497
Yolo	2,298	1,201	883	1,472	592	1,492	988	846	2,339
Total for Top 15 Counties	116,079	86,118	96,222	500,410	112,539	151,755	114,317	94,555	206,249
Percent of CA Total	69	74	77	93	79	80	77	83	91
Total Statewide Use	168,564	116,961	125,777	536,594	141,586	189,943	148,433	114,406	227,728

Table 3. Annual Cropland Use of Benomyl by Commodity (Pounds of Active Ingredient)

Crop	1990	1991	1992	1993	1994	1995	1996	1997	1998
Grapes	42,011	28,622	39,024	329,547	28,806	47,338	24,748	24,977	78,363
Almond	30,213	13,504	21,139	51,847	55,550	57,297	69,373	45,102	62,489
Tomatoes	1,016	415	319	316	837	944	587	1,166	61,082
All Other Nut Crops	526	409	589	1,367	1,909	10,843	10,029	6,234	38,279
Pome Fruit Crops	3,166	3,188	2,085	4,152	1,901	5,686	4,989	6,256	15,196
Small Fruits and Berries	66,979	8,752	11,465	9,314	7,860	12,212	8,952	9,394	11,763
Stone Fruit Crops	35,447	32,223	37,626	42,224	37,781	37,651	14,930	6,321	7,921
Celery	8,697	10,134	19,117	133,147	8,530	10,215	9,875	9,369	7,657
All Other Crop Uses	10,122	5,568	9,126	6,422	7,075	12,128	6,106	6,548	7,262
Citrus Fruits	97	82	12	39	19	19	52	2,058	5,839
Greenhouse/Nursery	24,838	16,418	4,358	1,626	929	480	381	674	670
All Non-Crop Uses	11,043	4,485	1,202	927	778	1,341	284	118	154
Total	234,156	123,799	146,063	580,927	151,974	196,154	150,305	118,217	296,675

Table 4. Annual Monthly Use of Benomyl (Pounds of Active Ingredient)

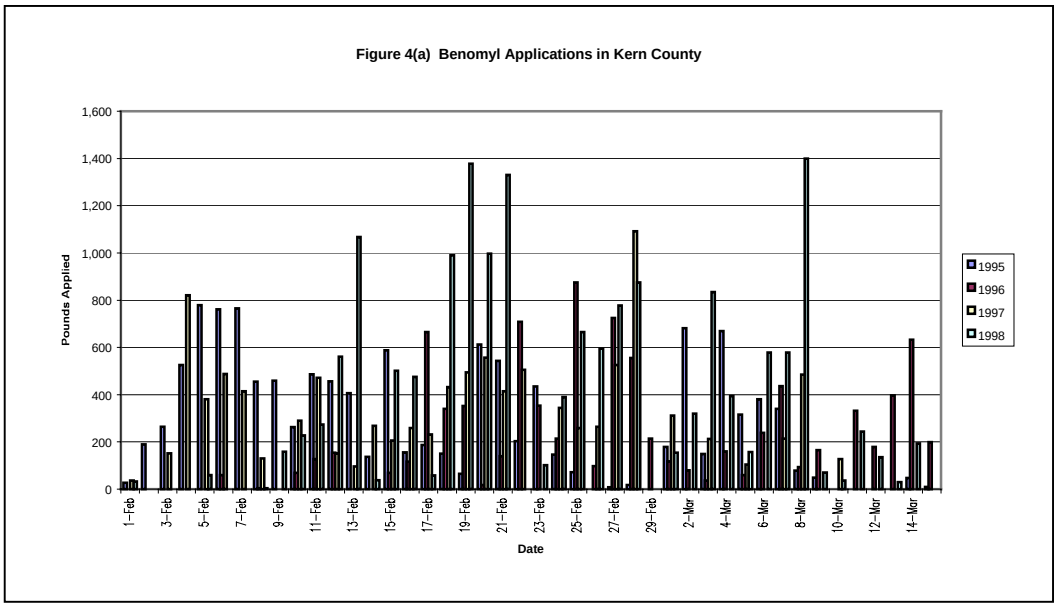
Month	1990	1991	1992	1993	1994	1995	1996	1997	1998
January	6,800	5,394	4,265	53,585	4,167	5,813	4,629	7,454	6,769
February	16,277	33,978	45,231	52,649	41,140	81,617	48,318	44,260	49,896
March	54,057	20,477	17,053	71,784	42,888	26,630	39,262	14,165	32,143
April	12,009	2,331	15,934	311,825	11,664	24,441	22,545	19,452	59,739
May	30,368	19,659	16,220	22,355	22,696	33,665	18,591	12,052	51,450
June	13,534	7,545	9,740	7,842	4,763	5,513	4,057	2,988	14,969
July	8,128	5,326	6,863	4,405	3,820	2,421	1,506	2,403	3,409
August	9,720	6,446	3,274	3,519	2,380	1,838	1,568	2,320	2,047
September	6,165	5,458	1,622	2,047	1,885	1,432	1,664	1,663	2,153
October	4,653	4,368	1,830	2,131	2,303	1,780	1,996	1,445	1,825
November	3,870	3,508	1,831	1,791	1,894	1,593	1,629	1,580	1,252
December	2,983	2,472	1,913	2,659	1,987	3,199	2,669	4,622	2,076
Total	*168,564*	*116,961*	*125,777*	*536,594*	*141,586*	*189,943*	*148,433*	*114,406*	*227,728*

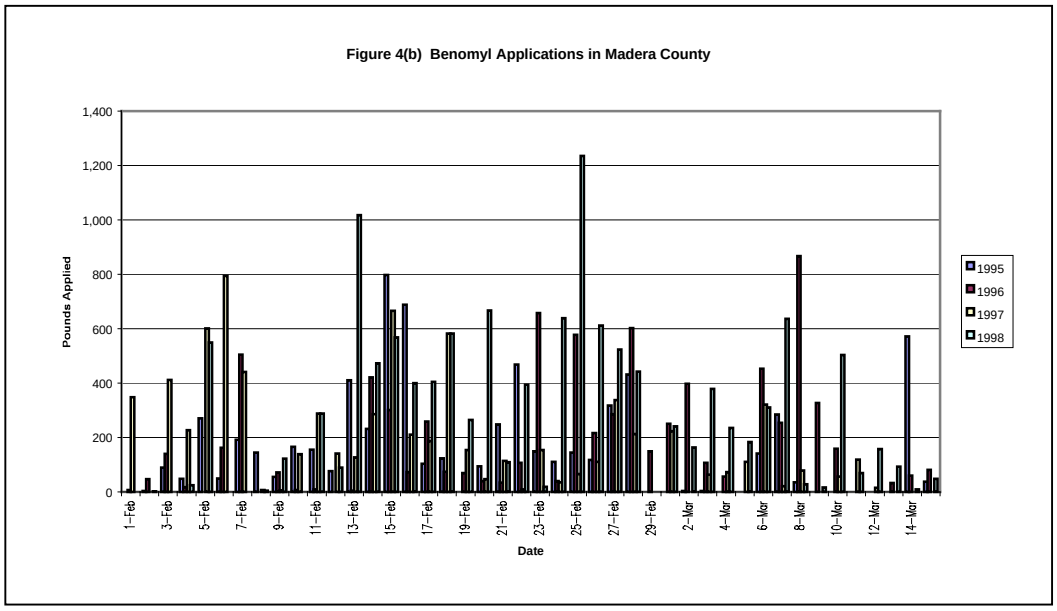
In Fresno, Kern, and Madera Counties, the predominant use has occurred consistently during the late winter and early spring, and was associated with applications to almonds. While this late winter peak occurred again in 1998, the period of peak use that year occurred during April in Madera and Kern Counties associated with applications to pistachios, and during May in Fresno County, associated with applications to grapes. Because the use in 1998 was inconsistent with past practices, and because 1999 PUR data is not yet available, it is difficult to predict if these April-May uses will regularly occur in future years.

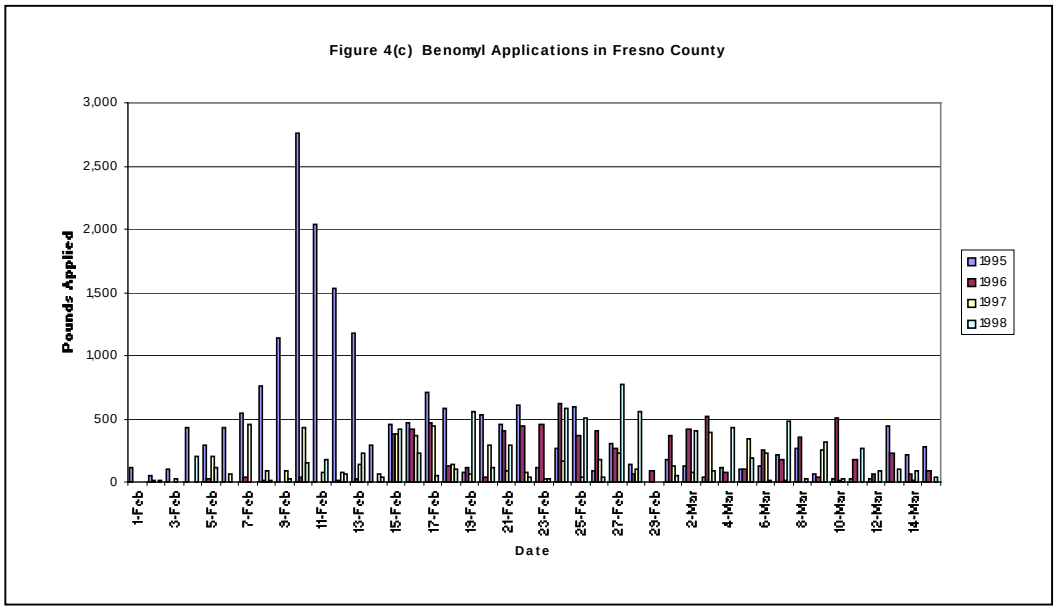
C. RECOMMENDATIONS

1. Ambient Air Monitoring

The historical trends in benomyl use suggest that monitoring should occur over a 30- to 45-day sampling period during the late winter in the Central Valley, in Fresno, Madera, or Kern Counties. Figure 4(a) shows Kern County's applications generally began in early February and tail off by mid-March. Alternatively, monitoring may be possible in Fresno or Madera Counties during the same period. Figures 5(a-e) display the areas of benomyl use by section in the Central Valley from 1994-1998, respectively. Three to five sampling sites should be selected in relatively high-population areas or in areas frequented by people (e.g., schools or school district offices, fire stations, or other public buildings). Samples should be collected and analyzed for benomyl (as carbendazim, if necessary) and BIC. Sampling sites should be located near almond growing areas. At each site, twenty to thirty discrete 24-hour samples should be taken during the sampling period. Background samples should be collected in an area distant to benomyl applications. Target 24-hour quantitation limits of at least 0.05 µg/m³ for benomyl (as carbendazim), and 8.1 µg/m³ for n-butyl isocyanate are recommended.







DPR recommends close coordination with the county agricultural commissioner to select the best sampling sites and periods. Replicate (collocated) samples are needed for five dates at each sampling location. In addition to the primary sampler, one collocated sampler should be run on those days. The date chosen for replicate samples should be distributed over the entire sampling period. They may, but need not be, the same dates at every site. Field spike samples should be collected at the same environmental conditions (e.g., temperature, humidity, exposure to sunlight) and experimental conditions (e.g., air flow rates) as those occurring at the time of ambient sampling. Additionally, we request that you provide in the ambient monitoring report: 1) the

proximity of the sampler to treated or potentially treated fields, including the distance and direction, and 2) the distance the sampler is located above the ground.

2. Application-Site Air Monitoring

The historical trends in benomyl use and product label information suggest that a typical agricultural application-site air monitoring study could be conducted in Fresno, Madera, or Kern County during the same months as the ambient study, in association with an application to grapes or almonds. The benomyl product labels offer several methods for application, including chemigation, and boom and air blast sprayers. DPR does not have a preference for the type of application method monitored. Ideally, monitoring should occur at a site using the highest allowed rates of use (i.e., about 6.0 pounds per acre), however, growers typically apply 1 pound per acre for almonds and stone fruits, and 1-2 pounds per acre for grapes. Rarely do applications exceed 3 pounds per acre.

DPR recommends close coordination with the county agricultural commissioner to select the best sampling sites and date. Again, samples should be collected and analyzed for benomyl (as carbendazim, if necessary) and BIC. Ideally, the monitoring study should include samples taken before, during, and for 72 hours following application, according to the following schedule:

Sample period begins:	**Sample duration time**
Background (pre-application)	Minimum 12 hours
During application	Length of application time
End of application	1 hour
1 hour post-application	2 hours
3 hours post-application[1]	3 hours (or up to 1 hour before sunset)
6 hours post-application[1]	6 hours (or up to 1 hour before sunset)
1 hour before sunset	Overnight[2] (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	24-hour (until 1 hour after sunrise)

[1] These samples and sample duration times may be adjusted depending on length of application time. The important issue is to take at least one 3-6 hour sample between the end of the 2-hour sample and dusk (one hour before sunset).

[2] All overnight samples must include the period from one hour before sunset to one hour after sunrise.

Occasionally, a pesticide application may occur all day long over the course of two or more days. In these instances, please collect a sample during the daily application, and an overnight sample between the end of the daily application and the start of application the next morning. Following the end of the application, begin collecting samples according to the above schedule, beginning with the 1-hour sample. Again, some sample time durations may be adjusted according to the

time remaining between end of application and dusk. Regardless of application duration, the study should include at least one 1-hour sample taken immediately following the end of application, at least one 2-4 hour sample (taken following the 1-hour sample), and all overnight samples must include the time period from one hour before sunset to one hour following sunrise.

The selected field should be 10 acres in area, or larger. A minimum of four samplers should be positioned, one on each side of the field. A fifth sampler should be collocated at one position. Since benomyl is extensively used in the area, background samples should collect enough volume to achieve the recommended target 24-hour quantitation limit of at least 0.05 $\mu g/m^3$ for benomyl (as carbendazim), and 8.1 $\mu g/m^3$ for BIC. Ideally, samplers should be placed a minimum of 20 meters from the field. Field spike samples should be collected at the same environmental conditions (temperature humidity, exposure to sunlight) and experimental conditions (similar air flow rates) as those occurring at the time of sampling.

Additionally, we request that you provide in the monitoring report: 1) an accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that the sampler is positioned from the field; 2) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, and other obstacles; 3) meteorological data collected at a minimum of 15-minute intervals including wind speed and direction, humidity, and air temperature, and comments regarding degree of cloud cover; and 4) the elevation of each sampling station with respect to the field, and the orientation of the field with respect to North (identified as either true or magnetic North).

D. SAFETY RECOMMENDATIONS

The benomyl product label warns that benomyl may irritate eyes, nose, throat, and skin. The label cautions that benomyl may cause a temporary allergic skin reaction in a few susceptible persons, which should be treated as an allergic dermatitis.

Monitoring personnel should use proper protective equipment to prevent exposure to the dust, vapors or spray mist. According to the product labels, proper protective equipment for applicators includes long-sleeved shirt and long pants, waterproof gloves and chemical-resistant footwear plus socks, and a dust/mist filtering respirator for outdoor exposures. Additional protective equipment includes a cartridge respirator equipped with a filter cartridge approved for use with pesticides, protective eyewear, and chemical-resistant headgear for overhead exposure. Monitoring personnel should refer to the label of the actual product used for further precautions.

Figure 5(a) Benomyl Use in the Central Valley
(February 1 through March 15, 1994)

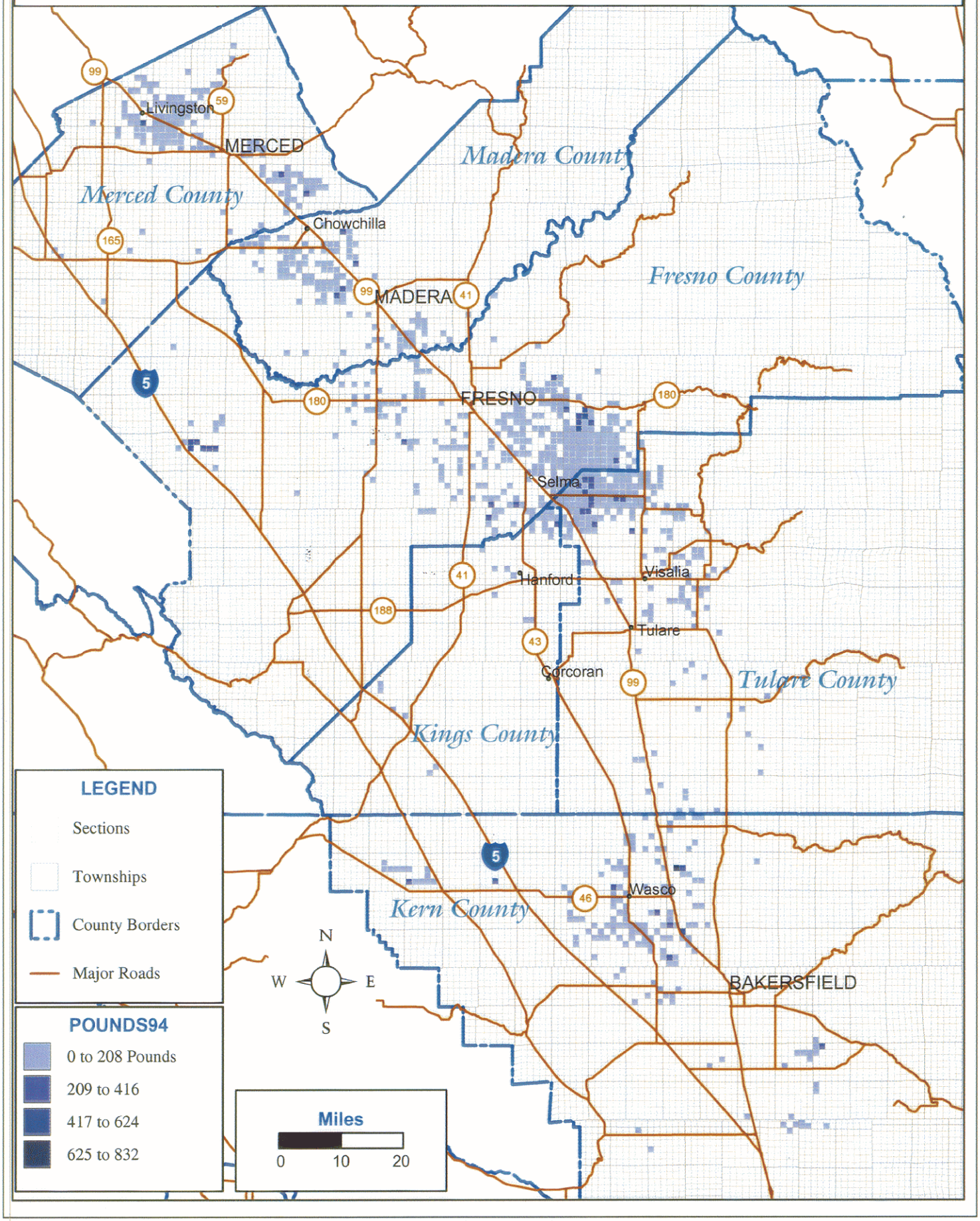


Figure 5(b) Benomyl Use in the Central Valley
(February 1 through March 15, 1995)

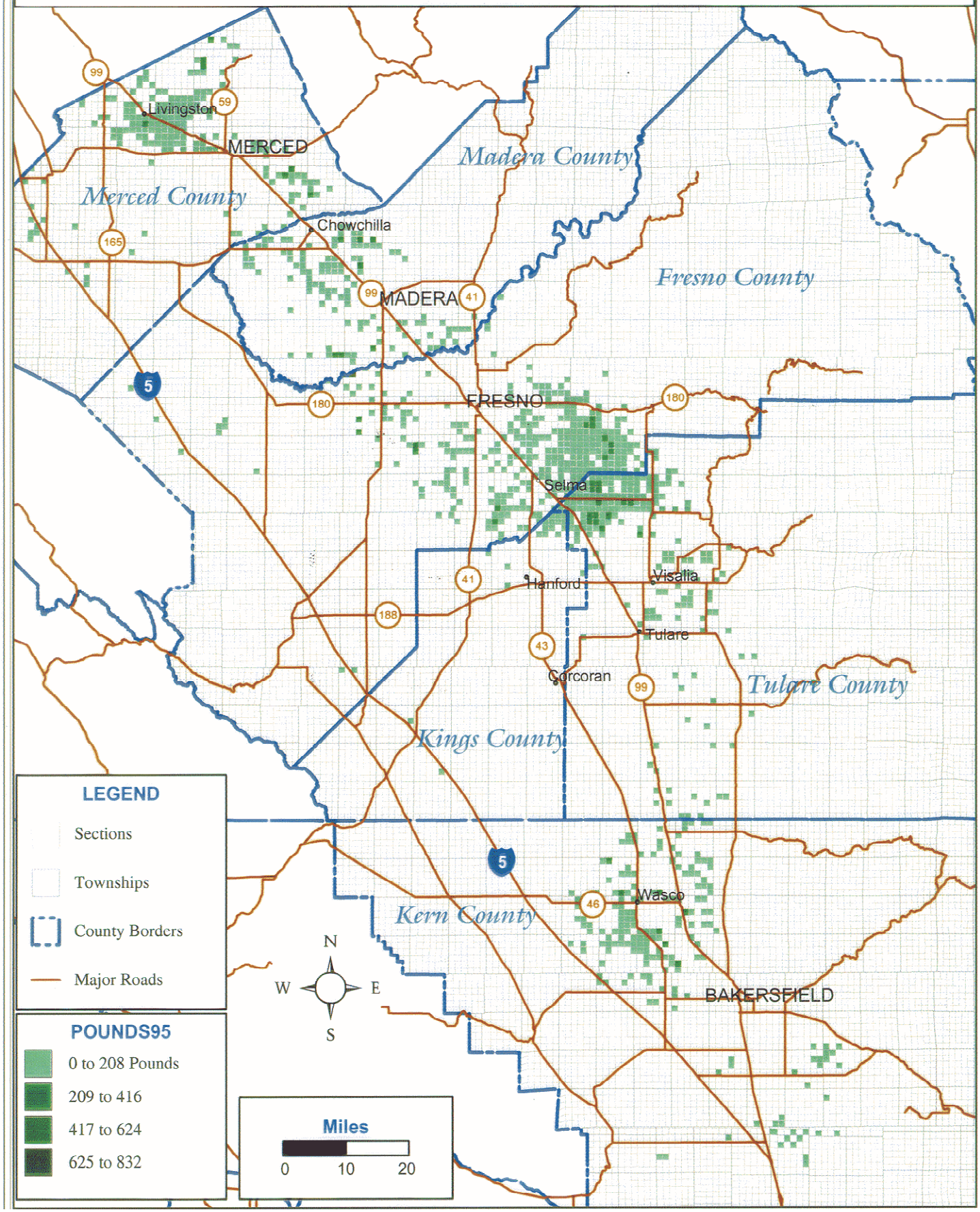


Figure 5(c) Benomyl Use in the Central Valley
(February 1 through March 15, 1996)

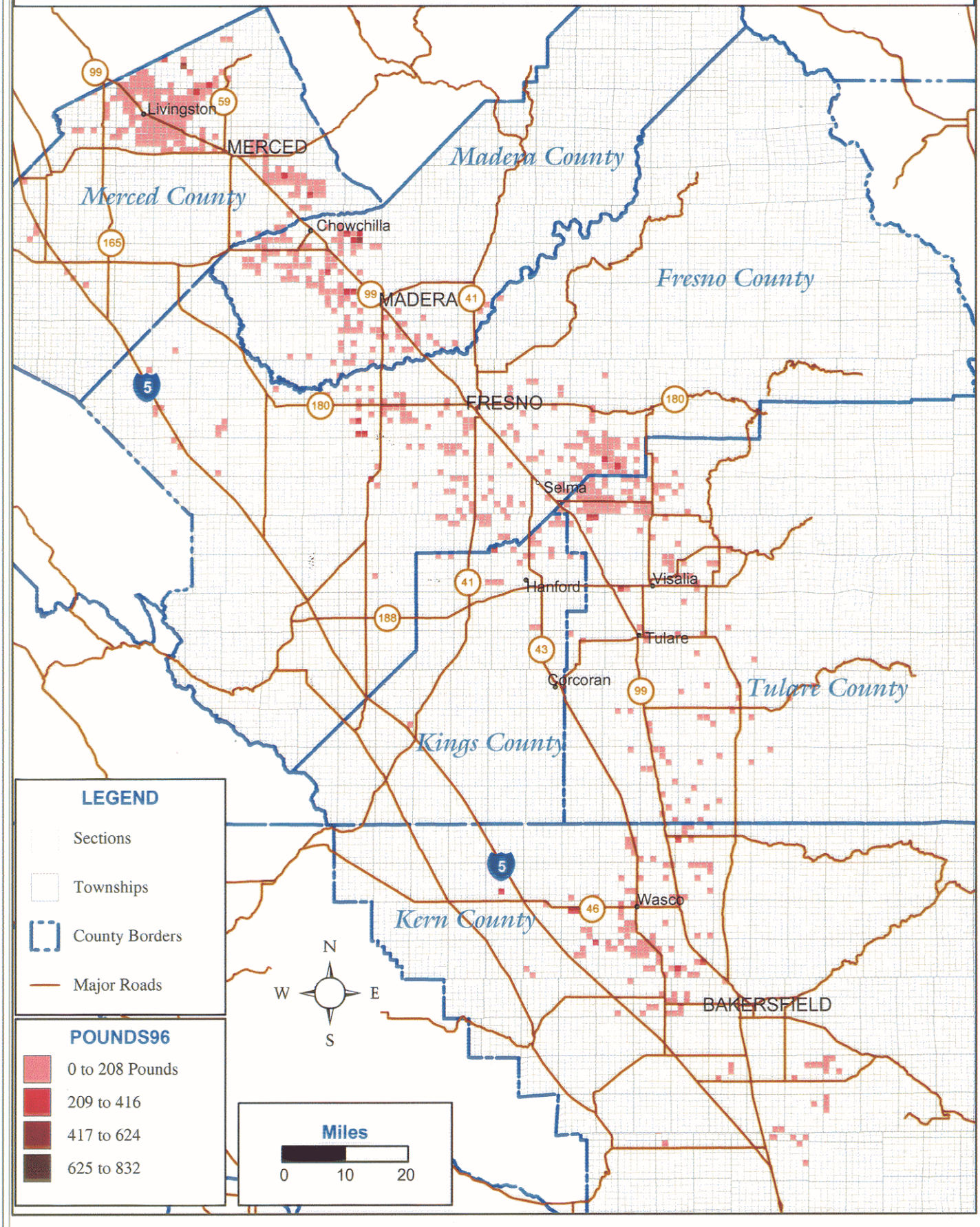


Figure 5(d) Benomyl Use in the Central Valley
(February 1 through March 15, 1997)

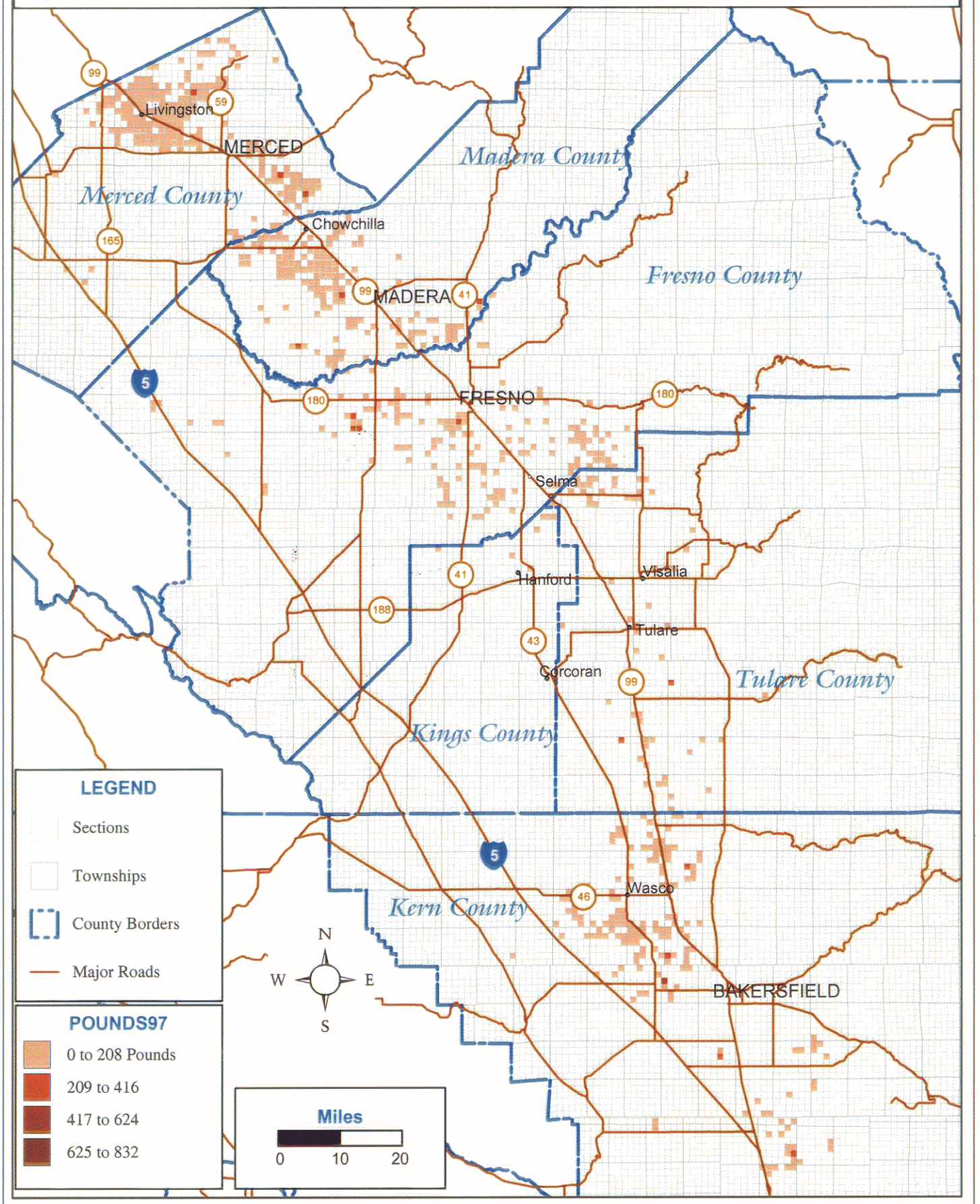
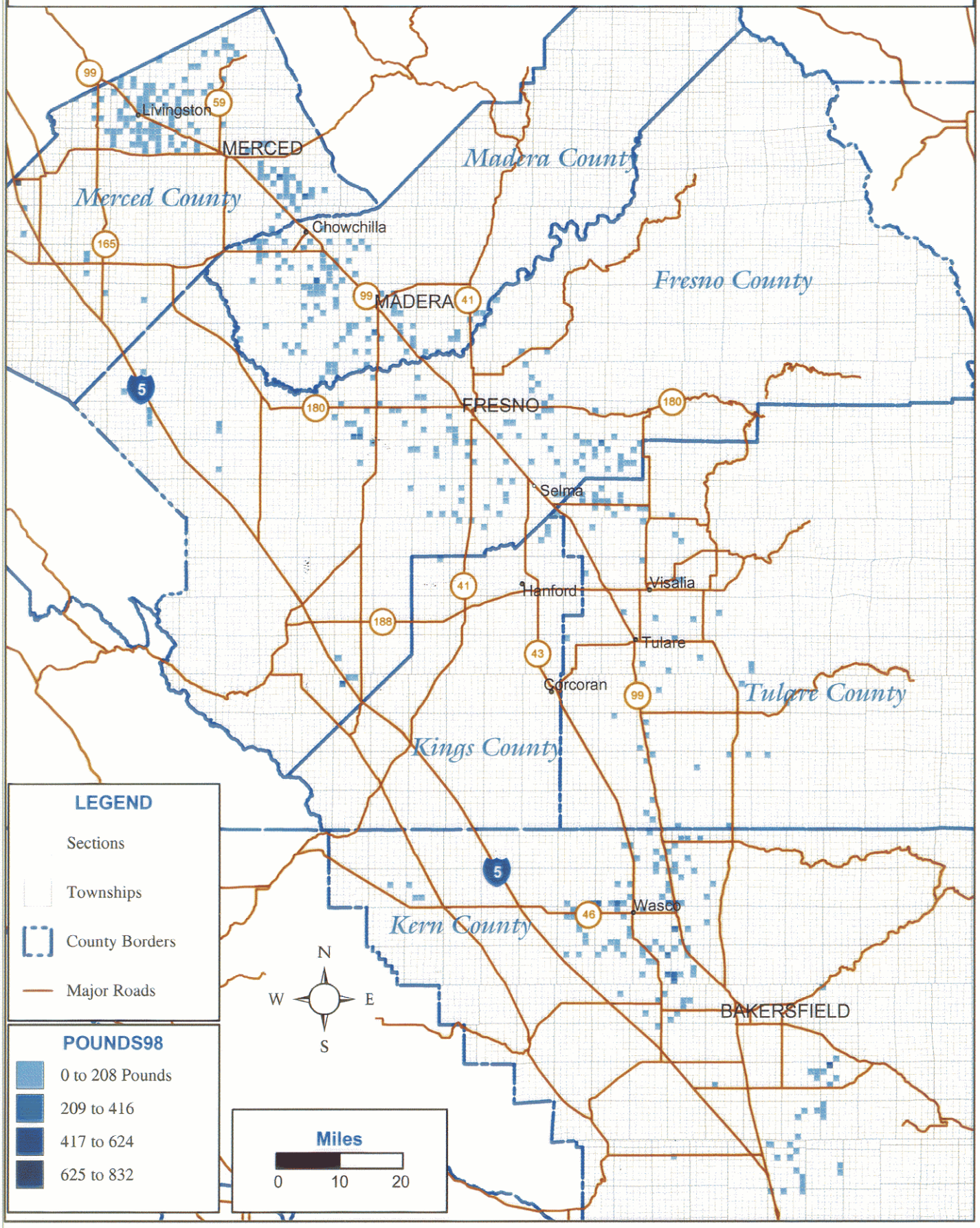


Figure 5(e) Benomyl Use in the Central Valley
(February 1 through March 15, 1998)



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